

# PATENT ABSTRACTS OF JAPAN

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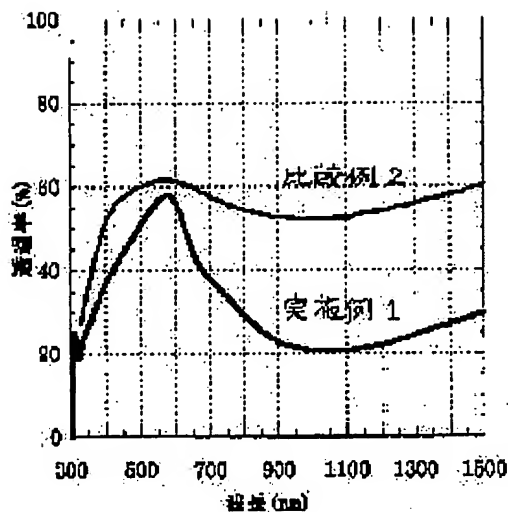
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**(54) SHIELDING MATERIAL AGAINST HEAT RAY, AND COATING LIQUID  
AND HEAT RAY SHIELDING FILM USING THAT**



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a shielding material against heat rays having high transmittance and low reflectance for light in a visible ray region and having low transmittance and high reflectance for light in a near infrared region, to provide a base body, and to provide a film in which the conductivity of the film can be controlled to about  $>10^6 \Omega/\text{unit sq.}$ , and to provide a coating liquid to form the film by easy coating method.

SOLUTION: This shielding material against heat rays contains fine particles of borides of metals selected from La, Pr, Nd, Ce, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W and having  $\leq 100 \text{ nm}$  average particle size. A coating liquid for a heat ray shielding film has dispersion of the heat ray shielding material, and contains one or more of ruthenium oxide fine particles or iridium oxide fine particles having  $\leq 100 \text{ nm}$  average particle

size. Then the heat ray shielding film is obtained by applying and heating the coating liquid above described on a base body.

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[Claim(s)]

[Claim 1] The heat ray shielding material containing the boride particle of 100nm or less of mean particle diameters of one sort chosen from the group of La, Pr, Nd, Ce, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W, or two sorts or more of metals.

[Claim 2] The heat ray shielding material containing one or more sorts in the boride particle of 100nm or less of mean particle diameters of one sort chosen from the group of La, Pr, Nd, Ce, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W, or two sorts or more of metals, the ruthenium oxide particle of 100nm or less of mean particle diameters, and the oxidization iridium particle of 100nm or less of mean particle diameters.

[Claim 3] The heat ray cover equipment containing a heat ray shielding material according to claim 1 or 2.

[Claim 4] Application liquid for heat ray cover film formation with which the heat ray shielding material according to claim 1 or 2 was distributed in the resin binder.

[Claim 5] Application liquid for heat ray cover film formation with which one or more sorts in the partial hydrolysis polymerization object of a heat ray shielding material according to claim 1 or 2, silicon and a zirconium, titanium, the metal alkoxide of aluminum, or a metal alkoxide were distributed in the resin binder.

[Claim 6] The heat ray cover film containing a heat ray shielding material according to claim 1 or 2.

[Claim 7] The multilayer heat ray cover film with which silicon, a zirconium, titanium, and the oxide film containing one or more sorts in the metallic oxide of aluminum were further formed on the heat ray cover film containing a heat ray shielding material according to claim 1 or 2.

[Claim 8] The multilayer heat ray cover film with which the resin film was further formed on the heat ray cover film according to claim 6 or 7.

[Claim 9] The heat ray cover film according to claim 6 to 8 whose difference of the maximal value of permeability and the minimal value permeability has the maximal value in the wavelength of 400-700nm, and has the minimal value in the wavelength of 700-1800nm, and is 15 points or more by percentage.

[Claim 10] The heat ray cover film according to claim 6 to 9 whose surface-electrical-resistance values are more than 106ohms / \*\*.

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[Translation done.]

## DETAILED DESCRIPTION

[0001]

[The technical field to which invention belongs] this invention relates to the heat ray shielding material used for the transparent or translucent base material which needs various heat ray cover functions of glass, and plastics and others, such as apertures, such as vehicles, a building, an office, and a common residence, a telephone booth, a show window, a lamp for lighting, and a transparent case, the equipment using this, application liquid, and a heat ray cover film.

[0002]

[Description of the Prior Art] Considering as a heat reflective glass by making a heat component into the method of removing and decreasing from sources of an extraneous light, such as sunlight and an electric bulb, conventionally using the material which reflects the wavelength of visible / infrared region in a glass front face was performed. And metallic oxides, such as FeOX, CoOX, CrOX, and TiOX, and the metallic material which has free electrons, such as Ag, Au, Cu, nickel, and aluminum, so much have been chosen as the material for heat ray reflection.

[0003] However, with such material, there was a property which also reflects or absorbs the light of a light field simultaneously in addition to the near infrared ray which contributes to a thermal effect greatly, and there was a fault to which a visible light transmittance falls. In the transparent base material used for building materials, a vehicle, a telephone booth, etc., the high permeability of a light field was needed, when using such material, in order to make a visible light transmittance high, thickness had to be made very thin, therefore being formed membranes and used for the very thin thin film of 10nm level using the physical forming-membranes methods, such as spray baking, CVD, or a spatter, a vacuum deposition method, has usually been performed.

[0004] These membrane formation methods needed large-scale equipment and the vacuum facility, and the problem was in productivity and large area-ization, and they were high. [ of the membranous manufacturing cost ]

[0005] Moreover, if these films tend to make thickness thin and it is going to make permeability high, a heat ray cover property will fall, thickness is thickened conversely, and a film will become dark if a heat ray cover property is made high. Furthermore, if it is going to make high these material heat ray cover properties, there is an inclination which becomes high simultaneously, and the reflection factor of a light field would also give appearance [ GIRAGIRA / appearance ] like a mirror, and will have spoiled the fine sight.

[0006] Furthermore, there are many to which membranous conductivity becomes high with such material. When membranous conductivity was high, the electric wave of a cellular phone, TV, radio, etc., etc. was reflected, it became non-receipt and there was a fault, such as causing an electromagnetic interference in a circumference area.

[0007] In order to improve the above-mentioned conventional fault, as a membranous physical property, the reflection factor of the light of a light field was low, and the reflection factor of the light of a near infrared region was high, and membranous conductivity needed to form the film controllable 106ohms / more than \*\* in general. However, the material which forms such [ conventionally ] a film or such a film was not known.

[0008] A visible light transmittance is high and an antimony content tin oxide (ATO) and

tin content indium oxide (ITO) are known as a material with a heat ray cover function. Such material had the comparatively low rate of a visible light reflex, and although the appearance [ GIRAGIRA / appearance ] was not given, the reflection and the absorption effect of these films / in / the near-infrared region near the light / it is in a long wavelength side comparatively, and ] of a near-infrared region did not have enough plasma wave length. Moreover, when these films were formed by the physical forming-membranes method, there was a fault which membranous conductivity goes up and reflects an electric wave.

[0009]

[Problem(s) to be Solved by the Invention] Then, it solves the trouble of the above-mentioned conventional technology, the permeability of this invention of the light of a light field is high, and its reflection factor is low. A heat ray shielding material with the low permeability of the light of a near infrared region, and a high reflection factor, the equipment using this, and the application liquid that can form membranes by the simple applying method, without conductivity using the physical forming-membranes method of high cost for a film controllable 106ohms / more than \*\* in general further in the above-mentioned property, It aims at offering the heat ray cover film using this.

[0010]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention persons variously paying attention to the boride which holds a free electron so much as a property of the material itself by ultrafine-particle-izing this and producing the equipment and film which were distributed highly as a result of examination The phenomenon of having both discovered plasma reflection strong against the near-infrared region near a light field for the maximum of permeability to a light field, and coming to have the minimum of permeability in it was found out, and this invention was completed.

[0011] That is, the heat ray shielding material of this invention is characterized by containing the boride particle of 100nm or less of mean particle diameters of one sort chosen from the group of La, Pr, Nd, Ce, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W, or two sorts or more of metals.

[0012] Moreover, other heat ray shielding materials of this invention are characterized by containing one or more sorts in the boride particle of 100nm or less of mean particle diameters of one sort chosen from the group of La, Pr, Nd, Ce, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W, or two sorts or more of metals, the ruthenium oxide particle of 100nm or less of mean particle diameters, and the oxidization iridium particle of 100nm or less of mean particle diameters.

[0013] Moreover, the heat ray cover equipment of this invention is characterized by containing the heat ray shielding material of the composition of one of the above.

[0014] Moreover, the application liquid for heat ray cover film formation of this invention is characterized by distributing the heat ray shielding material of the composition of one of the above in a resin binder.

[0015] Moreover, other application liquid for heat ray cover film formation of this invention is characterized by distributing one or more sorts in the partial hydrolysis polymerization object of the heat ray shielding material of the composition of one of the above, silicon and a zirconium, titanium, the metal alkoxide of aluminum, or a metal alkoxide in a resin binder.

[0016] Moreover, the heat ray cover film of this invention is characterized by containing

the heat ray shielding material of the composition of one of the above.

[0017] Moreover, the multilayer heat ray cover film of this invention is characterized by forming silicon, a zirconium, titanium, and the oxide film containing one or more sorts in the metallic oxide of aluminum further on the heat ray cover film of the above-mentioned composition.

[0018] Moreover, you may form a resin film further on these.

[0019] According to the above-mentioned this invention, permeability can have the maximal value in the wavelength of 400-700nm, and can have the minimal value in the wavelength of 700-1800nm, the heat ray cover film whose difference of the maximal value of permeability and the minimal value is 15 points or more by percentage can be realized, and the heat ray cover film whose surface-electrical-resistance values are more than 106ohms / \*\* can be realized.

[0020]

[Embodiments of the Invention] As a boride particle used for this invention A hoe-ized lanthanum (LaB<sub>6</sub>), hoe-ized plastic SEOJIUMU (PrB<sub>6</sub>), Hoe-ized neodium (NdB<sub>6</sub>), a HOU-ized cerium (CeB<sub>6</sub>), a HOU-ized yttrium (YB<sub>6</sub>), A titanium boride (TiB<sub>2</sub>), a zirconium boride (ZrB<sub>2</sub>), a HOU-ized hafnium (HfB<sub>2</sub>), Particles, such as hoe-ized vanadium (VB<sub>2</sub>), a hoe-ized tantalum (TaB<sub>2</sub>), hoe-ized chromium (CrB, CrB<sub>2</sub>), hoe-ized molybdenum (MoB<sub>2</sub>, Mo<sub>2</sub>B<sub>5</sub>, MoB), and a HOU-ized tungsten (W<sub>2</sub>B<sub>5</sub>), are mentioned as the typical thing.

[0021] Moreover, although it is desirable that the front face has not oxidized as for the boride particle used for this invention, it is not avoided to some extent that the object usually obtained has oxidized in many cases slightly, and surface oxidization takes place at the distributed process of a particle. However, there is no change in the effectiveness which discovers a heat ray shielding effect also by that case.

[0022] Although such a large heat ray shielding effect that the integrity as a crystal is high is obtained, a boride particle will discover a heat ray shielding effect, if the fundamental combination inside a particle consists of combination of a metal and boron even if it seems that crystallinity produces a diffraction peak [ low and very broadcloth in an X diffraction ].

[0023] Particles, such as a diacid-ized ruthenium (RuO<sub>2</sub>), ruthenium \*\*\*\* (Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub>), a ruthenium acid bismuth (Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>), diacid-ized iridium (IrO<sub>2</sub>), an iridium acid bismuth (Bi<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub>), and iridium \*\*\*\* (Pb<sub>2</sub>Ir<sub>2</sub>O<sub>6.5</sub>), are mentioned to the particle of the ruthenium oxide used for this invention, and oxidization iridium as the typical example. Stably as an oxide, these particles hold a lot of free electrons, and have a very effective heat ray cover function.

[0024] Although the above-mentioned boride particle, a ruthenium oxide particle, and an oxidization iridium particle are the powder colored ashes black, tea black, green black, etc., in the state where particle size distributed in the thin film and the transparent equipment sufficiently small compared with visible light wave length, visible light-transmission nature produces them to a film or an equipment. However, infrared light cover ability can be held sufficiently strongly.

[0025] the plasma frequency according [ although this reason is not understood in detail, the free electron in these particles has many amounts, and ] to the free electron plasmon of the interior of a particle, and a front face -- exactly -- visible - it is thought that it is because the heat ray of this wavelength field is alternatively reflected and absorbed since

it is in the near-infrared neighborhood

[0026] According to the experiment, by the film which distributed these particles sufficiently finely and uniformly, permeability has the maximal value in the wavelength of 400-700nm, and it has the minimal value in the wavelength of 700-1800nm, and it is observed that the difference of the maximal value of these permeability and the minimal value is 15 points or more by percentage further. If visible light wave length takes into consideration that it is 380-780nm and visibility is campanulate [ with a peak of near 550nm ], by such film, he can understand penetrating the light effectively, and reflecting and absorbing the other heat ray effectively.

[0027] In this invention, the mean particle diameter of the boride particle in application liquid, a ruthenium oxide particle, and an oxidization iridium particle has good 100nm or less. the ashes with which a characteristic permeability profile which was described above, i.e., permeability, had the maximal value in the wavelength of 400-700nm, it had the minimal value in the wavelength of 700-1800nm, a profile [ as / whose difference of the maximal value and the minimal value is 15 points or more by percentage ] was not obtained, but permeability decreased in monotone when the particle diameter became larger than 100nm -- it will become a sexy film Moreover, when a particle diameter is larger than 100nm, the condensation inclination of the particles in dispersion liquid will become strong, and will cause [ of a particle ] sedimentation. Since particles or those big and rough particles that were condensed 100 morenm or more serve as a source of light scattering, and cloudiness (Hayes) is produced on a film or they become the cause by which a visible light transmittance decreases, they are not desirable. Therefore, the mean particle diameter of the above-mentioned inorganic particle is 100nm or less. In addition, usually, although the minimum available particle size is an about 2nm particle economically, a minimum is not limited to this.

[0028] Especially the dispersion medium of the particle in application liquid is not limited, and is selectable according to the alkoxide in application conditions, application environment, and application liquid, a resin binder, etc. For example, it is usable, and the various kinds of organic solvents, such as water, and alcohol, the ether, ester, a ketone, may add an acid and alkali if needed, and may adjust pH. Furthermore, in order to raise the distributed stability of the particle in application liquid further, it is also possible to add various kinds of surfactants, a coupling agent, etc. Each addition at that time is 5 or less % of the weight preferably 30 or less % of the weight to a non-subtlety particle.

[0029] Since conductivity of the film when forming a film using this application liquid is performed along with the electric conduction path which went via the contact part of a particle, it is easy conductivity to be able to cut an electric conduction path partially by adjusting the amount of a surfactant or a coupling agent, and to reduce membranous conductivity to the surface-electrical-resistance value 106ohms / more than \*\*.

[0030] Moreover, conductivity is controllable also by adjusting the content of the partial hydrolysis polymerization object of silicon, a zirconium, titanium, the metal alkoxide of aluminum, or these metal alkoxide, or a synthetic-resin binder.

[0031] The distributed method of the above-mentioned particle can be arbitrarily chosen, if it is the method which a particle distributes in a solution uniformly. For example, methods, such as using a bead mill, a ball mill, and a sand mill and carrying out ultrasonic distribution, can be mentioned.

[0032] A plastic resin, glass, etc. of the shape of the shape of a tabular and a sheet and a

film can be used for the heat ray shielding material of this invention also as an additive at the time of manufacturing transparent equipments, such as an interlayer of a glass laminate. In the case of equipment manufacture, many of boride particles take cautions to oxidize or decompose at 500-700 degrees C.

[0033] On a base material, the above-mentioned particle deposits the heat ray cover film of this invention with high density, it forms a film, and the silicon contained in application liquid, a zirconium, titanium, the metal alkoxide of aluminum, the partial hydrolysis polymerization object of these metals, or a resin binder is effective in raising the binding property to the base material of a particle after an application and hardening, and raising a membranous degree of hardness further. Moreover, the degree of hardness and weatherability of the binding capacity to a membranous base material and a film which make a particle a principal component are further raised by putting the coat which contains the adding-water part depolymerization object of metal alkoxides, such as silicon, a zirconium, titanium, or aluminum, or these metal alkoxide, or a resin further on the film obtained by doing in this way as the 2nd layer.

[0034] When silicon, a zirconium, titanium, the metal alkoxide of aluminum, the adding-water part depolymerization object of these metals, or a resin binder is not included in application liquid, the film obtained after applying this application liquid to a base material becomes the membrane structure which only the above-mentioned particle deposited on the base material. A heat ray shielding effect is shown with this, and it is [ the application liquid which contains silicon, a zirconium, titanium, the metal alkoxide of aluminum, the adding-water part depolymerization object of these metals, or a resin binder in this film further like the above is applied, a coat is formed, and ] good also as a multilayer. Since an application liquid component fills the gap which the particle of the 1st layer deposited and is formed by doing in this way, membranous space decreases, and a visible light transmittance improves, and the binding property to the base material of a particle improves.

[0035] As a method of binding the film which makes the above-mentioned particle a principal component with the coat which consists of silicon, a zirconium, titanium, a metal alkoxide of aluminum, or a adding-water part depolymerization object of these metals, although a spatter and a vacuum deposition are also possible, an advantage, like the easy and low cost of a membrane formation process is low to the applying method is effective. Application liquid has 40 or less desirable % of the weight in [ all ] a solution at the oxide conversion from which two or more sorts are included and the content is obtained [ one sort or ] after heating in water or alcohol in silicon, a zirconium, titanium, the metal alkoxide of aluminum, or the adding-water part depolymerization object of these metals. Moreover, it is also possible to add an acid and alkali if needed and to adjust pH. It is possible to produce oxide coats, such as silicon, a zirconium, titanium, and aluminum, easily by applying such liquid as the 2nd layer further on the film which makes the above-mentioned particle a principal component, and heating it.

[0036] Especially the method of application of the application liquid of this invention and the application liquid for coat formation used by this invention is not limited. For example, the spin coat method, a spray coating method, a dip coating method, screen printing, the roll coat method, flow coating, etc. should just be flatness and the method of applying uniformly thinly about processing liquid.

[0037] The base-material heating temperature after the application of the application



liquid containing the above-mentioned metal alkoxide and its adding-water part depolymerization object Since the polymerization reaction of the alkoxide contained in a paint film at less than 100 degrees C or its adding-water part depolymerization object remains in many cases by un-completing, and water and an organic solvent remain in a film and it becomes the cause of reduction of the visible light transmittance of the film after heating 100 degrees C or more heat desirable still more preferably above the boiling point of the solvent in application liquid.

[0038] What is necessary is just to make it harden according to each hardening method, when a resin binder is used. For example, what is necessary is just to leave it as it is after the application that what is necessary is just to irradiate ultraviolet rays suitably if it is ultraviolet-rays hardening resin, if it is a room-temperature-setting resin. For this reason, an application in the site to the existing windowpane etc. is possible.

[0039] As a binder component used for the application liquid of this invention, you may use the ORGANO silazane solution as application liquid for overcoats. The thing 100 degrees C or less is also marketed for the polymerization curing temperature by correction of a side chain radical, or addition of an oxidation catalyst, and the ORGANO SHIZARAN solution can make membrane formation temperature quite low, if these are used.

[0040] As a room-temperature-setting nature binder, it is also possible to use the thing of a commercial silicate system. After hardening forms the inorganic film of  $\text{SiO}_2$ , and is superior to a resin film in weatherability or film intensity.

[0041] Since the above-mentioned ultrafine particle is distributing by the material of this invention, and the film, there is little reflection in a light field compared with a film with the mirror-plane-like front face where the crystal filled the inside of a film precisely like the oxide thin film manufactured by the physical forming-membranes method, and it can avoid presenting the appearance [ GIRAGIRA / appearance ]. On the other hand, since it has a plasma frequency in a visible - near-infrared region as mentioned above, the plasma reflection accompanying this becomes large in a near-infrared region. This is a very desirable property. The multilayer of 1% or less of luminous reflectances can be easily obtained by forming a film of a low refractive index like  $\text{SiO}_2$  or  $\text{MgF}$  on the particle distribution film of this invention to suppress reflection of a light field further.

[0042] In the application liquid of this invention, in order to raise permeability, you may mix ultrafine particles, such as ATO, ITO, and an aluminum addition zinc oxide, further. Since absorption in the near-infrared-ray field near the light will increase if these transparent ultrafine particles increase an addition, the high heat ray cover film of a visible light transmittance is obtained. Moreover, if the application liquid of this invention is added in the liquid which distributed ultrafine particles, such as ATO, ITO, and an aluminum addition zinc oxide, conversely, while coloring a film, the heat ray shielding effect can also be assisted. In this case, a heat ray shielding effect can be assisted with merely few additions to ITO used as a subject etc., a sharp reduction of the initial complement of ITO is possible, and the cost of liquid can be lowered.

[0043] In order to also give the cover function of ultraviolet rays detrimental to a human body to the material of this invention, an equipment, application liquid, and a film with a heat ray cover function, you may add one sort, such as particles, such as titanium oxide of an inorganic system, and a zinc oxide, a cerium oxide, a benzophenone of an organic system, and a benzotriazol, or two sorts or more.

[0044] Since the application liquid of this invention is not what forms the target heat ray cover film using the decomposition or the chemical reaction of an application component by the heat at the time of baking, it can form the transparency film of the uniform thickness by which the property was stabilized.

[0045] Thus, although manufacture of the equipment which has a heat ray shielding effect by mixing the material of the above-mentioned inorganic particle suitably, and a film is possible according to this invention, since such particle material is inorganic material, even if weatherability is very high compared with an organic material, for example, it uses it for the part which sunrays (ultraviolet rays) hit, degradation of a color or many functions is hardly produced.

[0046]

[Example] The example of this invention is explained with the example of comparison below.

[0047] (Example 1) 8g [ of LaB6 particles of 67nm of mean particle diameters ] and diacetone alcohol (DAA) 80g, water, and dispersant optimum dose were mixed, ball mill mixture was carried out for 100 hours using the zirconia ball with a diameter of 4mm, and 100g of LaB6 dispersion liquid was produced. Let this be A liquid. 50g of ethyl-silicate solutions which prepared the ethyl silicate 40 by Tama chemical-industry incorporated company which are 4 - a pentamer with average degree of polymerization by 6g, ethanol 31g, 8g of 5% hydrochloric-acid solution, and 5g of water, and 800g [ of water ] and ethanol 300g were mixed and stirred well, and 1150g of ethyl-silicate mixed liquor was prepared. Let this be B liquid.

[0048] The 1.0% and LaB6/SiO2 ratio mixed and stirred A liquid and B liquid at a rate which is set to 4:1, and LaB6 concentration produced application liquid. Let this be C liquid. Rotation was stopped, after dropping 15g of this C liquid from the beaker on the 200x200x3mm soda lime sheet glass substrate rotated by 145rpm and shaking it off for 3 minutes as it was. This was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained.

[0049] The spectral characteristic of the formed film was measured using the Hitachi spectrophotometer. The transparency profile of the film of this example using LaB6 particle is shown in drawing 1 . The maximal value of permeability was in 580nm, the minimal value was near 1055nm, the difference of the maximal value and the minimal value was as large as 38 points enough, and 54.6% of visible light transmittances was obtained as a value of film net based on JIS-R -3106.

[0050] The transparency color of the film by this example was a beautiful dark green color. Moreover, the rate of a visible light reflex was as low as 2.2%, and the feeling of a flash of a film surface like a commercial heat reflective glass was not sensed at all.

[0051] Furthermore, it turns out that  $3.2 \times 10^{11}$  ohms / \*\* is obtained when the surface-electrical-resistance value of this film is measured using the Mitsubishi Chemical surface-electrical-resistance meter, and there is no problem in electric wave permeability since the membrane-resistance value is sufficiently high.

[0052] (Example 1 of comparison) It became 38.8%, when 340-1800nm spectral transmittance was measured and it asked for the visible light transmittance according to JIS-R -3106 about the heat ray reflective bronze glass of marketing produced by the physical forming-membranes method of high cost compared with the applying method. Moreover, the rate of a visible light reflex was very as high as 34.2%, and was presenting

the appearance of the shape of a mirror [ GIRAGIRA / appearance / shape ]. Moreover, the surface-electrical-resistance value of a film surface was as low as 83ohms / \*\*, and the problem was in electric wave permeability and reflection nature.

[0053] (Example 2) After carrying out the spin coat of the C liquid produced in the example 1 as the 1st layer of sheet glass, rotation was continued for 3 minutes as it was, it continued, and rotation was stopped, after dropping from the beaker 15g of silicate liquid which diluted B liquid with ethanol so that it might become 0.9% by SiO<sub>2</sub> solid-content conversion on sheet glass and continuing rotation for 3 minutes further. Thus, the glass substrate of the applied two-layer film was put into the 180-degree C electric furnace, and the two-layer film which heats for 30 minutes and is made into the purpose was obtained.

[0054] The spectral characteristic of the formed film was evaluated like the example 1. While the visible light transmittance went up with 56.2%, the rate of a visible light reflex became 1.7%, and the reflected light was stopped further. Furthermore, the black tape was stuck on the rear face, and when the reflection from a rear face was lost and measured, the rate of a visible light reflex became 0.5%, and became the appearance near non-reflecting glass. The position of the maximum and the minimal value of the permeability of this film is almost the same as the monolayer in an example 1, and a hamper's is clear in the same heat ray shielding effect.

[0055] The same method estimated the maximum and the minimal value of the visible light transmittance of the film formed in the following examples 3-14 and examples 2-3 of comparison, and permeability, and the surface-electrical-resistance value that it stated to the example 1, they were summarized also including the result of examples 1 and 2, and were shown in Table 1.

[0056] (Example 3) 8g [ of LaB<sub>6</sub> particles of 67nm of mean particle diameters ] and isophorone 80g, water, and dispersant optimum dose were mixed, ball mill mixture was carried out for 100 hours using the zirconia ball, and 100g of LaB<sub>6</sub> isophorone dispersion liquid was produced. Let this be D liquid. As a binder, 50 % of the weight of epoxy resins was dissolved in the isophorone, and the epoxy resin binder solution was produced. Let this be E liquid. Application liquid was produced, as the weight ratio of LaB<sub>6</sub> and an epoxy resin was set to 70:30 1.4% of the weight of the whole, D liquid, E liquid, and ethanol were mixed and stirred powerfully, like the example 1, application liquid was produced, the solid content of LaB<sub>6</sub> and an epoxy resin formed and heated it, and the film was obtained.

[0057] (Example 4) As a binder, the room-temperature-setting type silicate liquid X-40-9740 made from Shin-etsu silicone was used instead of B liquid, application liquid was produced like the example 1, membranes were formed, and the film was obtained. However, heating evaluated the thing used as the dryness film by neglect for two days within [ of 25 degrees C ] a room temperature, without carrying out.

[0058] (Example 5) As a binder, the LaB<sub>6</sub> isophorone dispersion liquid (D liquid) and the xylene which used the cold cure type poly [ by N.E.CHEMCAT CORP. ] perhydro silazane solution instead of E liquid, and showed it to the example 3 were mixed and stirred, and the LaB<sub>6</sub>/SiO<sub>2</sub> ratio made this application liquid, as LaB<sub>6</sub> concentration was set to 4:1 1.0%. Membranes were formed like the example 1 using this, it heated with the 80-degree C electric furnace, and the film was obtained.

[0059] (Example 6) In A liquid manufacture, PrB<sub>6</sub> particle of 75nm of mean particle diameters was used instead of LaB<sub>6</sub>, and also application liquid was prepared completely

like the example 1, this was formed and heated, and the target film was obtained.

[0060] (Example 7) In A liquid manufacture, CeB6 particle of 58nm of mean particle diameters was used instead of LaB6, and also application liquid was prepared completely like the example 1, this was formed and heated, and the target film was obtained.

[0061] (Example 8) In A liquid manufacture, YB6 particle of 54nm of mean particle diameters was used instead of LaB6, and also application liquid was prepared completely like the example 1, this was formed and heated, and the target film was obtained.

[0062] (Example 9) In A liquid manufacture, TiB2 particle of 84nm of mean particle diameters was used instead of LaB6, and also application liquid was prepared completely like the example 1, this was formed and heated, and the target film was obtained.

[0063] (Example 10) In A liquid manufacture, TaB2 particle of 63nm of mean particle diameters was used instead of LaB6, and also application liquid was prepared completely like the example 1, this was formed and heated, and the target film was obtained.

[0064] (Example 11) In A liquid manufacture, the MoB particle of 59nm of mean particle diameters was used instead of LaB6, and also application liquid was prepared completely like the example 1, this was formed and heated, and the target film was obtained.

[0065] (Example 12) In A liquid manufacture, W2B5 particle of 85nm of mean particle diameters was used instead of LaB6, and also application liquid was prepared completely like the example 1, this was formed and heated, and the target film was obtained.

[0066] (Example 13) 15g [ of ruthenium oxide (RuO2) particles of 30nm of mean particle diameters ], 23g [ of N-methyl-2-pyrrolidones ] (NMP), and diacetone alcohol (DAA) 57g, water, and dispersant optimum dose were mixed, ball mill mixture was carried out for 100 hours using the zirconia ball with a diameter of 4mm, and 100g of RuO2 dispersion liquid was produced. The silicate liquid of B liquid was mixed and stirred and it considered as RuO2 distribution silicate liquid so that RuO2 concentration might become these RuO2 dispersion liquid with RuO2:SiO<sub>2</sub> = 4:1 1%. Let this be F liquid. A liquid was mixed in F liquid and it stirred enough in it so that it might become the weight ratio of RuO2:LaB<sub>6</sub> = 1.0:1.0, and application liquid was prepared in it. Using this application liquid, it was made to be completely the same as that of an example 1 membrane formation and heating, and the target film was obtained.

[0067] (Example 14) IrO2 particle of 28nm of mean particle diameters was used, and also IrO2:LaB6 mixture distribution silicate application liquid was produced completely like the example 11, this was formed and heated, and the target film was obtained.

[0068] In the above examples 1-14, about all films, the maximum of permeability is in the wavelength of 400-700nm, and the minimal value is in the wavelength of 700-1800nm, and it is observed that the difference of the maximal value and the minimal value is 15 points or more by percentage, and it is clear that these films are useful as a heat ray cover film. Moreover, the reflection factor in a light field is 8% or less, not all the films of an example had the mirror-like flash, surface-electrical-resistance values are more than  $8 \times 10^{10}$  ohms / \*\* by all films further, and it was confirmed that it is satisfactory in electric wave permeability.

[0069] (Example 2 of comparison) LaB6 of 137nm of mean particle diameters was used, and also LaB6 distribution silicate application liquid was produced completely like the example 1, this was formed and heated, and the target film was obtained. However, since this film had the too large diameter of a particle, it became the gray which cloudiness was large, and lacked in transparency (28% of Hayes values), and wore \*\*\*\* a little, and it

was judged that the difference of the maximal value and the minimal value was still as smaller as 12%, and it was difficult to present practical use as a heat ray cover film. [0070] (Example 3 of comparison) The ITO ultrafine particle of 22nm of mean particle diameters was used, and also ITO distribution silicate application liquid was produced completely like the example 1, this was formed and heated, and the target film was obtained. However, it turns out that this film cannot be used by this concentration (1%) at the purpose of permeability being 90% or more until it reaches [ from a light region ] a 1500nm infrared region, and covering a near infrared ray.

[0071]

[Table 1]

実施例	分散微粒子	バインダー	メーカコート膜	可視光透過率 (%)	透過率の極大波長 (nm)	透過率の極小波長 (nm)	極大値と極小値の差(%)	表面抵抗値 ( $\Omega/\square$ )
1	LaB <sub>6</sub>	シリケート	無し	54.8	580	1055	38	$3.2 \times 10^{11}$
2	LaB <sub>6</sub>	シリケート	シリケート	56.2	584	1060	34	$9.5 \times 10^{11}$
3	LaB <sub>6</sub>	エポキシ樹脂	無し	48.1	575	1039	23	$6.5 \times 10^{11}$
4	LaB <sub>6</sub>	常温硬化シリケート	無し	51.3	587	1104	32	$1.4 \times 10^{12}$
5	LaB <sub>6</sub>	シタゾン	無し	51.9	576	1033	42	$2.2 \times 10^{11}$
6	PrB <sub>6</sub>	シリケート	無し	55.7	594	1108	28	$6.4 \times 10^{11}$
7	CeB <sub>6</sub>	シリケート	無し	58.3	582	1046	38	$4.7 \times 10^{11}$
8	YB <sub>6</sub>	シリケート	無し	53.6	593	1061	34	$2.6 \times 10^{11}$
9	TiB <sub>2</sub>	シリケート	無し	63.4	493	986	29	$2.5 \times 10^{11}$
10	TaB <sub>2</sub>	シリケート	無し	52.8	608	1104	24	$2.5 \times 10^{12}$
11	MoB	シリケート	無し	49.6	456	978	28	$8.4 \times 10^{10}$
12	W <sub>2</sub> B <sub>5</sub>	シリケート	無し	58.2	591	1071	23	$5.3 \times 10^{11}$
13	LaB <sub>6</sub> +RuO <sub>2</sub>	シリケート	無し	64.3	583	1084	31	$7.8 \times 10^{11}$
14	LaB <sub>6</sub> +IrO <sub>2</sub>	シリケート	無し	62.5	589	1046	30	$8.6 \times 10^{11}$
比較例 1	—	—	無し	38.8	640	1000	8	83
比較例 2	LaB <sub>6</sub>	シリケート	無し	61.7	572	1024	12	$5.8 \times 10^{11}$
比較例 3	ITO	シリケート	無し	93.6	.	.	.	$8.3 \times 10^8$

[0072]

[Effect of the Invention] As shown in the above example, according to this invention, the permeability of the light of a light field was high, the reflection factor was low, and the application liquid in which conductivity can form a film controllable 106ohms / more than \*\* in general by the simple applying method further, without using the physical forming-membranes method of high cost, and the heat ray cover film using this have been offered in the heat ray shielding material with low permeability and a high reflection factor, the equipment using this, and the above-mentioned property of light of an The film of this invention is a heat ray cover film which does not have a surface feeling of a flash compared with a film conventionally, and was excellent also in electric wave permeability. Moreover, a cost side or the field of a large area film to industrial usefulness is high by using the application liquid of this invention.